Chapter 6
Sample Analysis Procedures

6.1 Overview

In the CTEPP study, more than 50 compounds were measured in 11 different types of sample matrices. Target compounds included two organophosphate (OP) pesticides, two OP metabolites, three pyrethroid pesticides, one pyrethroid metabolite, 10 organochlorine (OC) pesticides, three acid herbicides, nine polycyclic aromatic hydrocarbons (PAHs), two phthalates, three phenols, 17 polychlorinated biphenyls (PCBs), seven PAH metabolites, and one triazine. (Note that two carbamates, propoxur and bendicarb were originally included on the list of target pollutants but were later removed due to the study's analytical methods being incompatible for these pollutants.) The target pollutants and their metabolites were divided into two groups, neutral and acidic, based on their chemical properties. According to sample media, various extraction and cleanup methods were employed for these pollutants/metabolites in each group. The neutral and acidic pollutants and OP metabolites that were measured in the environmental and personal samples, except urine, are listed in Tables 6.1.1 and 6.1.2, respectively[1]. The target acidic pollutants/metabolites that were measured in urine are listed in Table 6.1.3. With the exception of creatinine in urine samples, Battelle performed all analyses of CTEPP field samples. No cross-checks by independent laboratories were used to confirm measured levels in some samples.

Both neutral and acidic pollutants as well as OP metabolites were measured in air, indoor floor dust, soil, hand wipe, hard floor surface wipe, food preparation surface wipe, transferable residue (PUF), and child food samples. Adult food samples were analyzed only for acidic pollutants and OP metabolites. Child food samples from North Carolina (NC) were analyzed for all neutral and acidic pollutants as well as one OP metabolite. Child food samples from Ohio (OH) were analyzed for all the target pollutants and two OP metabolites, except for the PCBs. Note that one OP metabolite, 3,5,6-trichloro-2-pyridinol (3,5,6-TCP), was measured in the NC samples and two OP metabolites, 3,5,6-TCP and 2-isopropyl-6-methyl-4-pyrimidinol (IMP), were measured in the OH samples. Drinking water samples were analyzed only for atrazine. Floor surface wipe samples, when collected to replace floor dust samples from homes without carpet, were analyzed for neutrals and acids. Additionally, food preparation surface wipe, hard floor surface wipe, and transferable residue samples were collected in homes where pesticides had been applied recently (within seven days of field sampling or during the 48-h monitoring period). In NC and OH, recent pesticide applications were only reported at homes and none at day care centers. The pesticides applied to the NC homes were all neutral pollutants, therefore,

[1]Participants were still able to purchase and apply both chlorpyrifos and diazinon at their residences or day care centers in NC and OH during the study.

Table 6.1.1 Neutral Target Pollutants for the CTEPP Study

Target Pollutants		
OP Pesticides	*trans*-Permethrin	**PCBs**[a]
Chlorpyrifos	**PAHs**	PCB 44 (2,2',3,5'-tetrachlorobiphenyl)
Diazinon	Benz[*a*]anthracene	PCB 52 (2,2',5,5'-tetrachlorobiphenyl)
OC Pesticides	Benzo[*a*]pyrene	PCB 70 (2,3',4',5-tetrachlorobiphenyl)
Aldrin	Benzo[*b*]fluoranthene	PCB 77 (3,3',4,4'-tetrachlorobiphenyl)
alpha-Chlordane	Benzo[*e*]pyrene	PCB 95 (2,2',3,5',6-pentachlorobiphenyl)
gamma-Chlordane	Benzo[*ghi*]perylene	PCB 101 (2,2',4,5,5'-pentachlorobiphenyl)
p,p'-DDE	Benzo[*k*]fluoranthene	PCB 105 (2,3,3',4, 4'-pentachlorobiphenyl)
p,p'-DDT	Chrysene	PCB 110 (2,3,3',4',6-pentachlorobiphenyl)
Dieldrin	Dibenz[*a,h*]anthracene	PCB 118 (2,3',4,4',5-pentachlorobiphenyl)
Endrin	Indeno[1,2,3-*cd*]pyrene	PCB 138 (2,2',3,4,4',5'-pentachlorobuphenyl)
Heptachlor	**Phthalates**	PCB 153 (2,2',4,4',5,5'-hexachlorobiphenyl)
Lindane	Benzylbutylphthalate	PCB 180 (2,2',3,4,4',5,5'-heptachlorobiphenyl)
Pentachloronitrobenzene	Di-*n*-butylphthalate	**Triazine**
Pyrethroid Pesticides	**Phenols**	Atrazine
Cyfluthrin	Bisphenol-A	
cis-Permethrin	Nonylphenol	

[a] Data were reported for 12 PCBs, but not for PCBs 10, 15, 28, 126, and 169. The data for the five PCBs were excluded because the presence of the volatile PCBs 10, 15, and 28 with the presence of closely eluted interference peaks could not provide useful information for Aroclor patterns and none of the PCBs 126 and 169 were detected in the samples.

Table 6.1.2 Acidic Target Pollutants and Metabolites for the CTEPP Study

Target Pollutants and Metabolites
OP Metabolites
2-Isopropyl-6-methyl-4-pyrimidinol (IMP) [a]
3,5,6-Trichloro-2-pyridinol (3,5,6-TCP)
Acid Herbicides
Dicamba
2,4-Dichlorophenoxyacetic acid (2,4-D)
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)
Phenols
Pentachlorophenol (PCP)

[a] IMP was measured only in the OH samples.

Table 6.1.3 Target Pollutants and Metabolites Measured in The CTEPP Urine Samples

Target Pollutants and Metabolites	
OP Metabolites	3-Hydroxybenz[*a*]anthracene [a]
2-Isopropyl-6-methyl-4-pyrimidinol (IMP)	3-Hydroxybenzo[*a*]pyrene[a]
3,5,6-Trichloro-2-pyridinol (3,5,6-TCP)	3-Hydroxychrysene
Pyrethroid Metabolite	6-Hydroxychrysene[a]
3-Phenoxybenzoic acid (3-PBA) [a]	6-Hydroxyindeno[1,2,3-*cd*]pyrene [a]
Acid Herbicides	1-Hydroxypyrene [a]
2,4-Dichlorophenoxyacetic acid (2,4-D)	**Phenols**
PAH Metabolites	Pentachlorophenol (PCP)
1-Hydroxybenz[*a*]anthracene	

[a] These metabolites were measured only in the OH samples.

the wipe and transferable residue samples were only analyzed for neutral pollutants. The pesticides applied to the OH homes were either neutral or acidic pollutants. Therefore, these OH samples were analyzed for either neutral or acidic pollutants/metabolites depending upon the type of pesticides that had been applied.

Environmental samples were solvent-extracted using Soxhlet extraction, sonication, accelerated solvent extraction (ASE), or refluxing techniques. Most samples required cleanup to remove potential interferences. Acidic compounds were derivatized using silylation or methylation, depending upon the compound. The specific gravity and creatinine concentrations of the urine samples were measured. Urine samples were then hydrolyzed under acidic conditions, extracted, derivatized, and cleaned up prior to analysis. Concentrated extracts of all samples were analyzed by gas chromatography/mass spectrometry (GC/MS) in the selected ion monitoring mode. Thirty different SOPs, as listed in Appendix A, were used due to the large variety of chemicals and matrices that were considered for extraction and analysis. Flow charts of the sample preparation and analysis methods used for all the target pollutants/metabolites in each sample media are given in Appendix C.

Quality control (QC) samples were analyzed to assess the overall quality of the analytical results. These QC samples included: (1) field and laboratory duplicates, (2) duplicate GC/MS analyses of sample extracts, (3) matrix spike samples (MSSs), and (4) field and laboratory blanks. Surrogate recovery standards (SRSs) were used to assess recovery in every sample.

6.2 Procedures for North Carolina and Ohio samples

The same sample analysis procedures were used to determine target pollutants and metabolites in environmental and personal samples collected in both NC and OH. As noted in Tables 6.1.2 and 6.1.3, a few additional acidic pollutants/metabolites were measured in the OH samples, along with the target compounds analyzed in the NC samples.

6.2.1 Extraction

Several types of samples required processing prior to extraction. Dust samples were sieved, and only the fine dust samples (<150 μm) were extracted. Any visible small rocks were removed from the soil samples, and then the sample was mixed with a glass rod before an aliquot was taken for extraction. Liquid food samples were thawed for 2 to 5 days in a refrigerator prior to extraction. Solid food samples were thawed (~2-5 days), homogenized with dry ice using a food processor (Hobart Food Chopper, 33"x19"x9.5"); and stored in glass jars at < -10°C for subsequent extraction. Urine samples were composited for each child and adult over the 48-h period at homes, except from homes with recent pesticide applications. The urine samples from the homes with recent pesticide applications were extracted individually. If the child attended day care, the urine samples collected from the day care center were not combined with the urine samples collected from the child's home. All other samples were processed as received from the field. Table 6.2.1 summarizes the SRSs and internal standards (ISs) used in the different types of samples. The SRSs were added to each sample prior to extraction, and the ISs were added to the concentrated sample extracts prior to GC/MS analysis. Table 6.2.2 summarizes the sample

preparation methods employed for each type of samples. Detailed preparation and extraction methods are described in CTEPP SOPs 5.12-5.23 and 5.27-5.29. Typically, all samples were extracted within 14 days of receipt.

Table 6.2.1 Surrogate Recovery Standards and Internal Standards for Chemical Analysis

Compound Class	Surrogate Recovery Standards	Internal Standards
Neutral Pollutants		
OP Pesticide	p,p'-DDE-d_4	Diazinon-d_{10}
OC Pesticide	p,p'-DDE-d_4	Phenanthrene-d_{10}, p,p'-Dibromobiphenyl
Pyrethroid Pesticide	p,p'-DDE-d_4	p,p'-Dibromobiphenyl
PAH	Dibenz[*a*,*h*]anthracene-d_{14}	p,p'-Dibromobiphenyl, Benzo[*e*]pyrene-d_{12}
Phthalate	Benzylbutylphthalate-d_4	p,p'-Dibromobiphenyl
Phenol	Bisphenol-A-d_6	p,p'-Dibromobiphenyl
PCB	2,2,4,5,5'-Pentachlorobiphenyl-C_{13}	Phenanthrene-d_{10}
Triazine [a]	NA [b]	Atrazine-d_5
Acidic Pollutants/Metabolites		
OP Metabolite	NA[b]	TCP-$C_{13}N_{15}$
Acid Herbicide	2,4-D-C_{13}	Dicamba-d_3
Phenol	2,4-D-C_{13}	Dicamba-d_3, TCP-$C_{13}N_{15}$
Acidic Pollutants/Metabolites in Urine		
OP Metabolite	NA[b]	TCP-$C_{13}N_{15}$
Pyrethroid Metabolite	2,4-D-C_{13}	Dicamba-d_3
Acid Herbicide	2,4-D-C_{13}	Dicamba-d_3
PAH Metabolite	2,4-D-C_{13}	Dicamba-d_3
Phenol	2,4-D-C_{13}	Dicamba-d_3

[a] Atrazine was measured only in drinking water samples.
[b] NA denotes not available.

Table 6.2.2 Summary of Sample Extraction Methods

Medium	Target Chemicals	Summary of Method
Air	Neutral pollutants	Soxhlet extract overnight (~14 h) with 80 mL dichloromethane (DCM); concentrate with Kuderna-Danish concentrator (KD); if cleanup is needed, solvent exchange to hexane; Florisil solid phase extraction (SPE) clean up with 18 mL of 15% ethyl ether (EE) in hexane; concentrate with KD.
	Acidic pollutants/metabolites	Soxhlet extract overnight (~14 h) with 80 mL acetonitrile (ACN); concentrate with KD; split sample extract for silylation and methylation. Silylate with 100 µL MTBSTFA at 70EC for 1 h. Methylate in 50 µL methanol with etheral diazomethane (diazald, carbitol, 37% aqueous KOH).
Dust/Soil	Neutral pollutants	0.5 g of dust or 1-2 g of soil, sonicate for 15 min with 2 x 10 mL of 10% diethyl ether in hexane; concentrate with KD; if cleanup is needed, Florisil SPE clean-up with 12 mL of 15% EE in hexane and 6 mL DCM; concentrate with KD.
	Acidic pollutants/metabolites	0.5 g of dust or 5 g of soil, accelerated solvent extraction (ASE) with acetone at 120EC and 2000 psi for 3 cycles of 10 min; concentrate with KD; split sample extract for silylation and methylation. Silylate with 100 µL MTBSTFA at 70EC for 1 h. Methylate in 50 µL methanol with etheral diazomethane; solvent exchange into isooctane; Florisil SPE clean up with 12 mL of 15% EE in hexane and 6 mL DCM; concentrate with KD.
Drinking Water	Atrazine	100 mL of drinking water, C18 SPE with 12 mL of 50% DCM in hexane; dry with sodium sulfate; filter through quartz fiber filter; concentrate with KD.
Solid Food	Neutral pollutants	12 g of solid food, ASE with DCM at 100EC and 2000 psi for 2 cycles of 5 min; dry with sodium sulfate; concentrate with KD; GPC clean-up with DCM; collect fractions F1 and F2 separately. Concentrate F2 with KD; F1: solvent exchange into ACN; ENVI-Carb clean up with 48 mL ACN; concentrate with KD or TurboVap
	Acidic pollutants/metabolites	8 g of solid food, ASE with methanol at 110EC and 2000 psi for 2 cycles of 5 min; concentrate with KD; extract with 15 mL MilliQ water; adjust to pH>12 with 40% KOH; extract with 3x20 mL hexane; discard hexane; acidify to pH<2 with conc. HCl; extract with 3x20 mL DCM; dry with sodium sulfate; concentrate with KD; split extract for silylation and methylation. Silylate with 100 µL MTBSTFA at 70EC for 1 h. Methylate in 50 µL methanol with etheral diazomethane.

Table 6.2.2 Summary of Sample Extraction Methods (cont.)

Medium	Target Chemicals	Summary of Method
Liquid Food	Neutral pollutants	30 mL of liquid food, reflux in 60 mL DCM for 1.5 h, filter, extract with 2x20 mL DCM, dry with sodium sulfate, filter, concentrate with KD, filter extract on micron acrodisc PTFE filter, GPC clean-up with DCM, collect fractions F1 and F2 separately. Concentrate F2 with KD. F1: solvent exchange into ACN; ENVI-Carb clean up with 48 mL ACN; concentrate with KD or TurboVap
	Acidic pollutants/metabolites	10 mL of liquid food, extraction method 1 or 2: *Method 1 for non-clear liquid food:* ASE with methanol at 110EC and 2000 psi for 2 cycles of 5 min; concentrate with KD for subsequent liquid-liquid partitioning as method 2. *Method 2 for clear liquid food:* liquid-liquid partitioning with 10 mL milliQ water and 10 mL sample, filter through quartz filter; add up to15 mL MilliQ water to resulting extract from either method 1 or 2; adjust to pH>12 with 40% KOH; extract with 3x20 mL hexane; discard hexane; acidify to pH<2 with concentrated HCl; extract with 3x20 mL DCM; dry with sodium sulfate; concentrate with KD; split extract for silylation and methylation. Silylate with 100 µL MTBSTFA at 70EC for 1 h. Methylate in 50 µL methanol with etheral diazomethane.
Dermal, Floor Surface, Food Preparation Wipes	Neutral pollutants	Soxhlet extract overnight (~14 h) with 300 mL DCM; filter on quartz fiber filter; concentrate with KD, if needed, Florisil SPE clean-up with 18 mL of 15% EE in hexane; concentrate with KD.
	Acidic pollutants/metabolites	ASE with acetonitrile (ACN) at 120EC and 2000 psi for 3 cycles of 5 min; concentrate with KD; split sample extract for silylation and methylation. Silylate with 100 µL MTBSTFA at 70EC for 1 h. Methylate in 50 µL methanol with etheral diazomethane. If needed, Florisil SPE clean-up with 18 mL of 15% EE in hexane; concentrate with KD.
Urine	Acidic pollutants/metabolites	1 mL urine: hydrolysis with 100 µL conc. HCl at 80EC for 1 h; add 1 mL of 20% NaCl solution, 1 mL chlorobutane (CB), and 10 µL of internal standard; mix and centrifuge; remove 800 µL of the extract and silylate with 100 µL MTBSTFA at 70EC for 1 h; transferred to GC vial. 10 mL urine: hydrolysis with 500 uL conc. HCl and 1 mL of CB at 80EC for 1 h; add 10 mL of 20% NaCl solution and extract with 3x10 mL DCM; concentrate with KD; methylate in 50 µL methanol with etheral diazomethane.

Prior to GC/MS analysis, two different derivatization methods, methylation and silylation, were used for the acidic compounds. Dicamba, 2,4-D, 2,4,5-T, 3-PBA, and hydroxy-PAHs were methylated using diazomethane. 3,5,6-TCP and IMP were silylated using N-(t-butyldimethylsilyl)-N-methyl-trifluoroacetamide (MTBSTFA). Pentachlorophenol (PCP) could be derivatized by methylation or silylation, and in early analyses the silylated derivative was used. However,
interferences were seen in some dust samples. Therefore, PCP was analyzed in most samples as the methyl derivative. After cleanup and derivatization, sample extracts were concentrated to 1 mL and spiked with internal standards, as shown in Table 6.2.2. Extracts were stored in a freezer at < -10EC until analysis. Typically, all samples were analyzed within 14 days of extraction.

6.2.2 Sample Analysis

All concentrated sample extracts and standard solutions were analyzed by 70 eV electron impact (EI) GC/MS. The Hewlett-Packard GC/MS was operated in the selected ion monitoring mode. Data acquisition and processing were performed with a ChemStation data system. The GC column was a DB-5 fused silica capillary (60 m x 0.32 mm, 0.25 µm film thickness). Helium was used as the GC carrier gas. The GC/MS operation conditions used for different types of samples are summarized in Table 6.2.3. Peaks monitored were the molecular ion peaks and their associated characteristic fragment ion peaks. Identification of the target compounds was based on their GC retention times relative to their internal standard and relative abundance of the monitored ions. Quantification of target compounds was based on comparisons of the integrated ion current response of the target ions to those of the respective internal standards using average response factors for the target compounds, generated from standard calibrations. The response factor was calculated using the following equation:

$$R_f = (A_s/A_{is}) \times (C_{is}/C_s)$$

where

A_s = area of quantification ion for target pollutant in the standard solution
A_{is} = area of quantification ion for internal standard in the standard solution
C_{is} = concentration of internal standard in the standard solution
C_s = concentration of target pollutant in the standard solution
Rf = response factor of target pollutant

The target pollutant concentration in the sample was calculated using the following equation:

$$C_s = (A_s/A_{is}) \times (C_{is}/R_{favg})$$

where

A_s = area of quantification ion for target pollutant in the sample extract
A_{is} = area of quantification ion for internal standard in the sample extract
C_{is} = concentration of internal standard in the sample extract
C_s = concentration of target pollutant in the sample extract
R_{favg} = average response factor of target pollutant

Table 6.2.3 Summary of GC/MS Operating Conditions

Medium	Target Chemicals	Summary of Method
Air, Dust, Soil, Solid Food, Liquid Food, Dermal Wipes, Floor Surface Wipes, Food Preparation Wipes, Transferable Residue	OP and OC pesticides, pyrethroid pesticides, PAHs, phthalates, and phenols	Injection volume: 1 µL Solvent delay: 7 min Inlet: 290EC Oven: 70EC (2 min hold), 15EC/min to 150EC, 6EC/min to 290EC Transfer line: 290EC
	PCBs	Injection volume: 1 µL Solvent delay: 7 min Inlet: 290EC Oven: 70EC (2 min hold), 20EC/min to 150EC, 4EC/min to 290EC (4 min hold) Transfer line: 290EC
	Acid herbicides and PCP	Injection volume: 1 µL Solvent delay: 7 min Inlet: 290EC Oven: 90EC, 8EC/min to 290EC Transfer line: 290EC
	OP metabolites (3,5,6-TCP and IMP), and PCP	Injection volume: 1 µL Solvent delay: 7 min Inlet: 290EC Oven: 90EC, 8EC/min to 290EC Transfer line: 290EC
Drinking Water	Triazine (atrazine)	Injection volume: 1 µL Solvent delay: 7 min Inlet: 290EC Oven: 70EC, 20EC/min to 190EC, 4EC/min to 215EC, 27EC/min to 290EC Transfer line: 290EC
Urine	Pyrethroid metabolite (3-PBA), 2,4-D, PAH metabolites, and PCP	Injection volume: 1 µL Solvent delay: 7 min Inlet: 290EC Oven: 90EC, 8EC/min to 290EC (5 min) Transfer line: 290EC
	OP metabolites (3,5,6-TCP, IMP)	Injection volume: 1 µL Solvent delay: 7 min Inlet: 290EC Oven: 90EC, 8EC/min to 290EC Transfer line: 290EC

6.2.3 Supplemental Measurements on Urine Samples

Creatinine concentration and specific gravity were measured in the urine samples so that comparisons of urine metabolite concentrations could be made from sample to sample on a common basis, considering that the dilution level of individual urine samples can vary greatly depending on the individuals' muscle activity, kidney efficiency, and the amount of water that they ingest. Creatinine is a byproduct of the breakdown of creatine and phosphocreatine, an energy storage compound in muscle. The more active the person, the greater the amount of creatinine excreted in the urine. The specific gravity is the weight of a known amount of urine compared to the weight of an equal amount of water. Specific gravity measures the kidney's ability to concentrate or dilute urine in relation to plasma. Because urine is a solution of minerals, salts, and compounds dissolved in water, the specific gravity of urine is greater than 1. Urine specific gravity increases as the urine becomes more concentrated.

Aliquots (10 mL each) of composited urine samples were removed for creatinine analysis. The non-composited urine samples were not analyzed for creatinine, because of the small sample size per void and the need to analyze the urine samples for parent compounds or metabolites. The urine sample aliquots were sent to the Ohio State University Clinical Laboratory for creatinine analysis. The method employed was the Jaffee Picric Acid, colorimetric method. Specific gravity measurements were performed on all composited and non-composited urine samples, using reagent strips purchased from Lab Essentials Inc. (Monroe, GA), Urine Reagent Strips (9-parameter). The reagent end of the strip was dipped into the urine sample. After one minute, the color of the test strip was compared to the standard color chart, and the specific gravity value was recorded.

6.2.4 Method Evaluation

6.2.4.1 Instrument Performance

The GC/MS system was calibrated with perfluorotributylamine according to the manufacturer's instructions, to verify that acceptable performance criteria were achieved, before analyzing any standard solutions and/or samples. A multi-point calibration curve (typically five points) was constructed with calibration standards for each sample set. An average response factor (Rf) of each target pollutant was generated from the multi-point calibration curve. The percent relative standard deviation (% RSD) of the calculated Rf values in all the calibration solutions was required to be within ± 25%. The calculated values of the standard solutions were checked to ensure that the relative percent difference (%RPD) was within ± 30% of the expected values. If the % RSD values of some compounds were greater than ± 25%, the GC/MS system was checked to determine the sources of this variation. Appropriate corrective actions (i.e., cleaning the source) were taken. The calibration standard solutions and the sample set were then re-analyzed, and another multi-point calibration curve was generated for quantification.

6.2.4.2 Method Performance

6.2.4.2.1 North Carolina Method precision was evaluated based on the results from duplicate samples and duplicate GC/MS analyses. One field duplicate air sample for neutral analysis, and one for acid analysis, were collected in the NC study. Duplicate NC samples for dust, soil, food and urine were duplicate aliquots of these samples. Duplicate wipe and transferable residue samples were not obtained because it was not feasible to obtain true duplicate samples for these sample media. For example, once a surface has been wiped or sampled with a PUF roller, there is no other equivalent surface from which a duplicate sample can be obtained. A summary of the mean and standard deviation (SD) values of the %RPD of the duplicate NC samples are given in Tables 6.2.4 through 6.2.6. For neutral pollutants in the multimedia samples, the mean %RPD ranged from 0 to 26%, except for PCB 52 for which the mean %RPD ranged from 0 to 36%. The mean %RPD for acidic pollutants/metabolites ranged from 0 to 16%. Duplicate GC/MS analyses were performed on randomly selected sample extracts for all sample media (the same sample extract was analyzed twice by GC/MS). Results of the mean and SD for the %RPD of the duplicate GC/MS analyses are summarized in Tables 6.2.7 to 6.2.9. The mean %RPD ranged from 0 to 9% for all neutral and acidic pollutants/metabolites.

Overall method accuracy was evaluated by measuring the recoveries of the MSSs and SRSs that had been spiked onto all field samples. Recoveries of the MSSs for dust, soil, liquid food, solid food, and urine samples were obtained from different aliquots of the corresponding spiked and non-spiked samples. Recoveries of the MSSs of air, wipe, and PUF samples were obtained from the spiked blank sample media. The mean and SD values of the recovery data from the NC matrix spike samples are summarized in Tables 6.2.10 to 6.2.12. Typical spiking levels of MSSs and SRSs by matrix are shown in these Tables. With few exceptions, satisfactory recoveries were obtained for most target pollutants/metabolites in all types of samples. Mean recoveries ranged from 54±6.5 to 130±6.5% for neutral pollutants. Mean recoveries ranged from 64±16 to 99±23% for acidic pollutants/metabolites. High background levels of the two phthalates were found in the non-spiked blank sample media as well as in the field samples. Consequently, the spiked levels of the two phthalates were not high enough in most of the matrix spike samples to provide satisfactory recovery data. For the same reason, satisfactory recoveries for target OP pesticides and PAHs could not be obtained in a few dust and soil samples. Interference peaks were observed for bisphenol-A, cyfluthrin, and *cis*-permethrin. Recovery data for these samples were not included in calculating the mean and SD as noted in Table 6.2.10. A *trans*-permethrin standard was not available at the early stage of the NC field study, thus some of the matrix spike samples did not contain this compound.

Recovery data of SRSs are summarized in Tables 6.2.13 to 6.2.15. Quantitative recoveries for the SRSs including *p,p'*-DDE-d_4, dibenz[*a,h*]anthracene-d_{14}, PCB101-C_{13}, and 2,4-D-C_{13} were obtained in most NC field samples. Recoveries for SRSs ranged from 56±9.5 to 120±18% for neutral pollutants and from 75±11 to 91±18%for acidic pollutant, 2,4-D-C_{13}. Interference peaks were observed for benzylbutylphthalate-d_4 and bisphenol-A-d_6, in some air, dust, soil, and wipe samples. Therefore, satisfactory recoveries were not obtained.

Field blanks and laboratory method blanks were used to assess background contamination from field sample handling and laboratory sample processing. Results of the neutral and acidic

pollutants/metabolites in field blanks and laboratory blanks from NC are summarized in Tables 6.2.16 to 6.2.17. Typically, field blanks were taken every other week during the sampling periods in each state. Field blanks for air, wipe, and PUF samples were unspiked sampling cartridges, precleaned wipes, and precleaned PUFs respectively. These cartridges, wipes, and PUFs were taken to the field and treated the same way as field samples, but were not exposed. Field blanks for dust/soil and liquid/solid food were empty containers that were used for collecting the respective samples and went through the same field handling procedures as field samples. Because the same kind of wipes was used for dermal wipes, floor surface wipes, and food preparation wipes, all the wipe samples shared the same field blanks. Dust and soil samples shared the same field blanks, because the same type of containers was used for these samples.

The reported median and SD values in Tables 6.2.16 and 6.2.17 were generated from the combined field blanks and laboratory blanks data. These tables do not include the pollutants/metabolites that were not detected in the blanks from all sample media. If the target pollutant/metabolite was detected in some of the blanks, the non-detected blank results were replaced by the method detection limit (MDL) divided by the square root of two for all media, except liquid food, in the determination of the median and SD values. Non-detected results for liquid food blanks were replaced by the MDL divided by ten. With few exceptions, most target pollutants/metabolites were not detected in the field blanks and laboratory method blanks. The median values of these pollutants/metabolites were below or close to the method detection limits in these blanks. Measurable amounts of bisphenol-A in wipe samples, and of the two phthalates in all sample media, were found in the field blanks and laboratory method blanks in NC. Therefore, background correction was performed for these samples, before the data were used for the statistical analysis discussed in Chapter 8 of this report. Two PUF method blanks (11% of all PUF samples) were analyzed for neutrals; one did not contain any detectable target pollutants except for the two phthalates. The other PUF blank contained few PCBs; visible particles were observed in this blank PUF, which were probably due to contamination in the laboratory. There were 29 (6.1% of total urine samples) method blanks, and 12 (2.5% of total urine samples) field blanks, which were collected and analyzed for target pollutants/metabolites in urine. None of the urine blanks had any detectable target compounds.

Only one target pollutant, atrazine, was measured in the drinking water samples, thus all QC data for the drinking water samples are summarized in Table 6.2.18. There was no SRS for the water samples, because atrazine-d_5 was used as an internal standard. Overall method precision was very good; the mean of the %RPD of duplicate water samples was 2.2 ± 3.5%, and a similar result was obtained from the duplicate GC/MS analyses. Average recovery of the matrix spike samples was 84 ± 20%. Trace amounts of atrazine were found in some of the blank samples.

Table 6.2.4 Results for Duplicate Samples for Neutral Pollutants - North Carolina

Pollutant	Air		Dust/Soil		Liquid Food		Solid Food	
Number of QC samples	2		30		10		6	
Percent of field samples	0.7		10		6.1		3.6	
	Relative Percent Difference, %							
OP Pesticides	mean [a]	SD	mean	SD	mean	SD	mean	SD
Chlorpyrifos	24	NA	14	27	-	-	-	-
Diazinon	- [b]	-	5.4	8.9	-	-	-	-
OC Pesticides								
Aldrin	-	-	1.2	3.1	-	-	-	-
alpha-Chlordane	1.3	NA [c]	4.2	5.6	-	-	-	-
gamma-Chlordane	9.3	NA	4.3	5.9	-	-	-	-
p,p'-DDE	-	-	1.7	4.2	-	-	4.4	6.9
p,p'-DDT	-	-	2.8	7.6	-	-	0.25	0.44
Dieldrin	-	-	3.0	9.3	-	-	-	-
Endrin	-	-	0.22	0.85	-	-	-	-
Heptachlor	4.2	NA	1.5	3.3	-	-	-	-
Lindane	7.4	NA	-	-	-	-	2.9	5.0
Pentachloronitrobenzene	-	-	-	-	-	-	-	-
Pyrethroid Pesticides								
Cyfluthrin	-	-	0.63	1.59	-	-	-	-
cis-Permethrin	-	-	3.1	4.9	1.3	2.4	2.5	3.4
trans-Permethrin	-	-	4.6	6.1	5.2	9.7	8.9	15
PAHs								
Benz[*a*]anthracene	-	-	21	23	0.76	1.7	4.5	4.0
Benzo[*a*]pyrene	-	-	14	12	-	-	3.6	1.8
Benzo[*b*]fluoranthene	-	-	14	11	-	-	5.3	0.45
Benzo[*e*]pyrene	-	-	17	14	-	-	1.9	0.95
Benzo[*ghi*]perylene	-	-	16	15	-	-	-	-
Benzo[*k*]fluoranthene	-	-	9.9	8.0	-	-	0.59	0.51
Chrysene	-	-	15	15	0.19	0.42	3.2	1.7
Dibenz[*a,h*]anthracene	-	-	9.6	12	-	-	-	-
Indeno[1,2,3-*cd*]pyrene	-	-	13	11	-	-	-	-
Phthalates								
Benzylbutylphthalate	6.0	NA	23	25	23	23	26	26
di-*n*-Butylphthalate	13	NA	20	26	18	9.4	18	11
Phenols								
Bisphenol-A	-	-	2.3	4.6	2.8	3.2	2.9	2.5
Nonylphenol	-	-	1.1	4.2	1.4	3.1	-	-
PCBs								
PCB 44	-	-	0.04	0.15	-	-	-	-
PCB 52	36	NA	1.5	3.4	-	-	-	-
PCB 70	-	-	0.67	2.2	-	-	-	-
PCB 77	-	-	-	-	-	-	-	-
PCB 95	7.8	NA	1.8	6.9	-	-	-	-
PCB 101	7.6	NA	1.9	6.4	-	-	-	-
PCB 105	-	-	1.2	4.5	-	-	-	-
PCB 110	-	-	0.71	1.8	-	-	-	-
PCB 118	-	-	1.2	2.5	-	-	-	-
PCB 138	-	-	0.04	0.14	-	-	-	-
PCB 153	-	-	0.51	1.5	-	-	-	-
PCB 180	-	-	0.76	2.9	-	-	-	-

[a] Only one duplicate air sample was collected for neutral pollutants; the reported mean value of RPD is the RPD value of the duplicate samples.
[b] - denotes that the target pollutant was below detection limit in all duplicate samples.
[c] NA denotes not applicable.

Table 6.2.5 Results for Duplicate Samples for Acidic Pollutants/Metabolites - North Carolina

Pollutant	Air		Dust/Soil		Liquid Food		Solid Food	
Number of QC samples	2		20		28		44	
Percent of field samples	0.7		6.7		9.8		15	
	Relative Percent Difference, %							
OP Metabolites	mean [a]	SD	mean	SD	mean	SD	mean	SD
3,5,6-TCP	16	NA [c]	8.0	8.9	5.8	7.0	7.7	6.5
Acid Herbicides								
Dicamba	- [b]	-	-	-	-	-	-	-
2,4-D	-	-	2.6	5.6	0.33	1.2	4.7	7.7
2,4,5-T	-	-	-	-	-	-	0.47	2.1
Phenols								
PCP	0.69	NA	4.8	4.4	-	-	1.3	3.5

[a] Only one air duplicate sample was collected for acidic pollutants; the reported mean value of RPD is the RPD for the duplicate samples.
[b] - denotes that the target pollutant was below detection limit in all duplicate samples.
[c] NA denotes not applicable.

Table 6.2.6 Results for Duplicate Samples for Urine Analysis - North Carolina

Pollutant	Urine	
Number of QC samples	26	
Percent of field samples	5.5	
	Relative Percent Difference, %	
OP Metabolites	mean	SD
IMP	- [a]	-
3,5,6-TCP	7.9	7.3
Acid Herbicides		
2,4-D	2.5	3.2
PAH Metabolites		
1-Hydroxybenz[*a*]anthracene	4.0	14
3-Hydroxychrysene	-	-
Phenols		
PCP	8.2	8.5

[a] - denotes that the target pollutant was below detection limit in all duplicate samples.

Table 6.2.7 Results for Duplicate Analyses of the Same Sample Extract for Neutral Pollutants - North Carolina

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
	PCB	Others	PCB	Others	PCB	Others	PCB	Others	PCB	Others	PCB	Others
Number of QC samples	24	28	38	34	36	42	34	34	30	26	-	2
Percent of field samples	7.9	9.2	13	11	12	15	21	21	18	16	0.0	11
	Relative Percent Difference, %											
OP Pesticides	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean [a]	SD
Chlorpyrifos	3.3	3.1	2.7	5.0	5.5	4.6	0.38	1.1	3.9	5.5	0.29	NA [b]
Diazinon	2.0	3.1	3.5	5.2	1.5	3.5	0.02	0.08	2.6	5.9	1.1	NA
OC Pesticides												
Aldrin	0.35	0.91	- [c]	-	0.42	1.9	-	-	0.52	1.9	-	-
alpha-Chlordane	2.4	2.9	4.0	6.2	2.8	5.5	-	-	0.56	1.3	-	-
gamma-Chlordane	2.1	3.0	3.1	4.3	1.8	2.6	-	-	0.85	2.1	-	-
p,p'-DDE	-	-	2.9	5.6	0.09	0.39	0.39	0.86	3.3	3.4	-	-
p,p'-DDT	0.34	1.3	0.62	1.3	0.11	0.36	-	-	0.50	1.8	-	-
Dieldrin	1.8	5.4	2.6	5.9	2.4	10	-	-	-	-	-	-
Endrin	1.5	2.8	0.89	2.2	0.02	0.10	-	-	-	-	-	-
Heptachlor	2.6	4.1	0.69	1.7	1.6	3.8	-	-	0.54	0.99	-	-
Lindane	-	-	0.08	0.33	0.90	3.1	-	-	0.00	0.00	-	-
Pentachloronitrobenzene	-	-	-	-	-	-	-	-	-	-	-	-
Pyrethroid Pesticides												
Cyfluthrin	0.21	0.78	1.4	3.9	0.99	2.4	-	-	-	-	0.05	NA
cis-Permethrin	1.9	3.6	7.4	13	5.9	6.9	0.60	1.7	0.43	1.2	3.5	NA
trans-Permethrin	2.0	3.4	4.7	5.5	7.7	8.1	0.61	1.7	0.33	0.67	0.33	NA
PAHs												
Benz[*a*]anthracene	3.2	4.9	4.8	5.2	3.1	4.4	0.21	0.85	2.6	3.8	7.8	NA
Benzo[*a*]pyrene	2.6	4.6	4.6	5.5	2.1	4.9	-	-	0.89	2.1	-	-
Benzo[*b*]fluoranthene	3.4	7.2	6.0	11	2.0	3.7	-	-	1.7	2.6	-	-
Benzo[*e*]pyrene	2.6	3.1	3.0	3.2	2.5	4.4	-	-	0.86	1.3	-	-
Benzo[*ghi*]perylene	4.0	6.1	5.1	6.3	3.6	7.2	-	-	-	-	-	-
Benzo[*k*]fluoranthene	2.4	2.9	4.6	4.8	1.9	5.3	-	-	1.2	2.3	-	-
Chrysene	3.3	5.6	3.3	3.0	2.7	4.5	0.05	0.22	0.74	1.2	-	-
Dibenz[*a,h*]anthracene	0.72	1.9	2.9	3.8	0.55	2.0	-	-	-	-	-	-
Indeno[1,2,3-*cd*]pyrene	5.6	7.2	6.4	6.9	3.6	9.0	-	-	-	-	-	-

Table 6.2.7 Results for Duplicate Analyses of the Same Sample Extract for Neutral Pollutants - North Carolina (cont.)

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
Phthalates	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Benzylbutylphthalate	7.6	10	8.9	11	7.3	8.0	2.0	1.6	5.8	7.4	3.1	NA
di-*n*-Butylphthalate	3.9	6.4	4.7	4.1	3.1	3.2	3.3	5.7	3.6	6.8	4.4	NA
Phenols												
Bisphenol-A	6.5	8.9	1.2	2.7	8.6	7.7	3.1	3.3	4.1	2.6	5.4	NA
Nonylphenol	0.71	2.7	2.7	8.5	1.3	4.4	0.14	0.59	0.1	0.34	-	NA
PCBs												
PCB 44	0.47	1.6	0.54	2.3	0.46	2.0	-	-	-	-	-	-
PCB 52	4.6	6.2	1.2	3.1	1.3	4.4	-	-	-	-	-	-
PCB 70	0.86	2.6	-	-	0.24	1.0	-	-	-	-	-	-
PCB 77	-	-	-	-	-	-	-	-	-	-	-	-
PCB 95	2.2	3.8	0.69	2.5	0.59	1.7	-	-	0.03	0.12	-	-
PCB 101	1.4	2.6	0.99	2.5	0.35	1.5	-	-	-	-	-	-
PCB 105	-	-	-	-	-	-	-	-	-	-	-	-
PCB 110	1.7	3.1	1.7	3.4	0.60	1.9	-	-	-	-	-	-
PCB 118	0.79	2.8	2.4	5.3	0.18	0.64	-	-	-	-	-	-
PCB 138	-	-	1.3	3.4	0.13	0.56	-	-	-	-	-	-
PCB 153	0.45	1.6	2.1	6.1	1.4	3.9	-	-	-	-	-	-
PCB 180	0.10	0.35	1.3	3.7	0.25	0.93	-	-	-	-	-	-

[a] Only one duplicate GC/MS analysis for OC, OP, PAH, PE, Phenols, and PY performed on the PUF sample; the reported mean value of RPD is the RPD of the duplicate GC/MS analyses.
[b] NA denotes not applicable.
[c] - denotes that the target pollutant was below detection limit in all duplicate GC/MS analyses.

Table 6.2.8 Results for Duplicate Analyses of the Same Sample Extract for Acidic Pollutants/Metabolites - North Carolina

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food	
	silylate	methylate	silylate	methylate	silylate	methylate	silylate	methylate	silylate	methylate
Number of QC samples	22	20	40	32	21	22	16	22	34	38
Percent of field samples	7.3	6.6	13	11	8.2	8.6	5.6	7.7	12	13
	Relative Percent Difference, %									
OP Metabolites	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
3,5,6-TCP	5.7	6.0	4.1	4.5	5.5	4.3	1.5	1.7	3.1	3.6
Acid Herbicides										
Dicamba	-[a]	-	2.3	7.0	-	-	-	-	0.99	2.1
2,4-D	2.4	7.0	1.6	2.7	0.89	2.9	-	-	2.8	4.0
2,4,5-T	0.12	0.37	-	-	-	-	-	-	-	-
Phenols										
PCP	7.9	6.2	5.3	4.7	1.5	2.7	-	-	0.15	0.64

[a] - denotes that the target pollutant was below detection limit in all duplicate GC/MS analyses.

Table 6.2.9 Results for Duplicate Analyses of the Same Sample Extract for Urine - North Carolina

Pollutant	Urine	
Number of QC samples	54	
Percent of field samples	11	
	Relative Percent Difference, %	
OP Metabolites	mean	SD
IMP	1.1	3.9
3,5,6-TCP	3.9	2.8
Acid Herbicides		
2,4-D	4.6	5.4
PAH Metabolites		
1-Hydroxybenz[*a*]anthracene	1.3	2.7
3-Hydroxychrysene	0.44	1.4
Phenols		
PCP	3.7	3.7

Table 6.2.10 Results for Matrix Spike Samples for Neutral Pollutants - North Carolina

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
Typical spike level, ng	50		20		20		50		50		50	
Number of QC samples	15		19		21		10		8		2	
Percent of field samples	4.9		6.4		7.3		6.1		4.8		11	
	Percent Recovery, %											
OP Pesticides	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Chlorpyrifos [a]	100	13	89	18	110	18	110	17	95	25	85	20
Diazinon [b]	81	9.5	80	12	96	17	54	6.5	58	18	84	3.5
OC Pesticides												
Aldrin	90	9.2	80	14	95	15	93	16	83	11	87	19
alpha-Chlordane	95	9.8	76	14	99	18	91	18	71	9.1	74	1.1
gamma-Chlordane	92	11	76	17	95	17	88	18	72	8.4	76	3.8
p,p'-DDE	96	13	80	14	96	18	88	18	80	11	84	0.33
p,p'-DDT	110	17	97	20	130	35	120	41	110	14	110	
Dieldrin	87	10	83	21	95	16	88	13	91	16	86	5.7
Endrin [c]	100	13	96	19	110	22	100	20	91	10	85	-
Heptachlor	100	15	96	23	100	21	100	28	96	18	89	12
Lindane	92	10	83	11	100	17	97	20	92	11	95	6.2
Pentachloronitrobenzene	97	13	75	14	110	22	120	31	110	17	78	7.9
Pyrethroid Pesticides												
Cyfluthrin [d]	100	15	100	19	110	16	64	12	88	13	91	23
cis-Permethrin [e]	120	17	100	31	110	20	88	15	97	14	82	6.4
trans-Permethrin [f]	-	-	-	-	-	-	86	25	78	14	-	-
PAHs												
Benz[*a*]anthracene	110	20	96	23	110	26	110	25	85	15	90	12
Benzo[*a*]pyrene	110	12	87	15	98	19	120	17	89	15	92	16
Benzo[*b*]fluoranthene	110	13	95	21	120	23	100	15	82	10	85	10
Benzo[*e*]pyrene	95	11	83	15	95	16	87	11	73	7.8	78	7.0
Benzo[*ghi*]perylene	93	11	89	19	91	16	110	15	95	12	77	1.8
Benzo[*k*]fluoranthene	110	14	87	16	100	20	110	14	81	9.7	85	4.8
Chrysene	100	15	86	19	100	22	93	20	71	9.2	96	17
Dibenz[*a,h*]anthracene	110	18	91	19	99	20	110	15	87	15	77	5.7
Indeno[1,2,3-*cd*]pyrene	99	15	93	20	95	20	110	18	89	15	77	7.7

Table 6.2.10 Results for Matrix Spike Samples for Neutral Pollutants - North Carolina (cont.)

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
Phthalates	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Benzylbutylphthalate [g]	-	-	110	28	-	-	74	24	67	13	-	-
di-*n*-Butylphthalate [h]	-	-	100	29	-	-	61	25	61	1.7	-	-
Phenols												
Bisphenol-A [i]	91	17	69	12	110	27	130	10	100	17	80	30
Nonylphenol [j]	100	16	89	22	120	16	130	9.5	125	14	85	31
PCBs												
PCB 44	92	14	79	13	100	16	90	13	74	12	86	7.8
PCB 52	91	14	81	16	100	16	88	11	75	13	87	5.5
PCB 70	93	11	80	13	110	17	95	12	81	18	91	8.4
PCB 77	100	12	88	15	110	19	100	16	89	8.7	98	24
PCB 95	89	13	74	12	100	17	86	13	78	23	81	12
PCB 101	92	13	78	12	100	17	91	14	79	18	91	8.7
PCB 105	100	13	87	18	120	22	99	18	82	9.7	100	23
PCB 110	97	14	81	17	110	19	100	12	77	12	97	15
PCB 118	99	13	86	17	120	23	100	16	86	20	97	23
PCB 138	100	16	86	17	110	22	96	18	73	9.4	100	25
PCB 153	97	13	85	16	120	21	96	17	74	8.8	97	25
PCB 180	110	16	89	21	120	27	97	19	78	16	110	19

[a] Data for two dust/soil samples were excluded because of low spike level.
[b] Data for one dust/soil sample was excluded because of low spike level.
[c] Data for one PUF sample was excluded because of matrix effect.
[d] Data for seven dust/soil, two wipe, six liquid food, and one solid food were excluded because of low spike level, or interference.
[e] Data for 12 dust/soil and five wipe samples were excluded because of low spike level or matrix effect.
[f] Trans-permethrin standard was included in the matrix spike solution in part of NC field study.
[g] Data for all air, wipe, and PUF as well as 15 dust/soil, seven liquid food, and six solid samples were excluded because of low spike level or interference.
[h] Data for all air, wipe, and PUF as well as 12 dust/soil, seven liquid food and six solid food samples were excluded because of low spike level or interference.
[i] Data for 12 dust/soil, 13 wipe, and two liquid food samples were excluded because of low spike level, or matrix effect.
[j] Data for four dust/soil, five wipe, and three liquid food samples were excluded because of matrix effect.

Table 6.2.11 Results for Matrix Spike Samples for Acidic Pollutants/Metabolites - North Carolina

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food	
Typical spike level, ng	50		50		50		50		50	
Number of QC samples	20		19		12		14		21	
Percent of field samples	6.6		6.4		4.7		4.9		7.1	
	Percent Recovery, %									
OP Metabolites	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
3,5,6-TCP	80	11	8	18	80	8.2	69	14	80	7.8
Acid Herbicides										
Dicamba	64	16	72	16	75	13	74	14	88	13
2,4-D [a]	67	18	76	23	77	15	80	15	92	15
2,4,5-T	69	15	78	19	74	15	80	14	99	14
Phenols										
PCP	99	23	78	26	69	11	67	14	78	14

[a] Data for four dust/soil samples were excluded because of low spike level or matrix effect.

Table 6.2.12 Results for Matrix Spike Samples for Urine Analysis - North Carolina

Pollutant	Urine	
Typical spike level, ng/sample	25	
Number of QC samples	32	
Percent of field samples	6.8	
	Percent Recovery, %	
OP Metabolites	mean	SD
IMP [a]	7.2	3.2
3,5,6-TCP	99	11
Acid Herbicides		
2,4-D	98	12
PAH Metabolites		
1-Hydroxybenz[*a*]anthracene [b]	92	22
3-Hydroxychrysene [b]	95	18
Phenols		
PCP	79	10

[a] Low recoveries were obtained for IMP because the analytical method used was developed for 3,5,6-TCP, not IMP.
[b] Data for three urine samples were excluded because of matrix effect or interference.

Table 6.2.13 Results for Surrogate Recovery Standards for Neutral Pollutants - North Carolina

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
Typical spike level, ng	50		50		20		50		50		50	
Number of QC samples	351		371		346		202		197		23	
Percent of field samples	110		120		120		120		120		130	
Percent Recovery, %												
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Benzylbutylphthalate-d_4 [a]	120	18	110	21	120	15	74	25	56	9.5	110	16
Bisphenol-A-d_6 [b]	110	21	73	22	110	19	110	21	100	21	55	19
Dibenz[*a*,*h*]anthracene-d_{14} [c]	110	18	87	19	99	19	110	22	88	21	87	11
p,p'-DDE-d_4	97	14	84	19	100	18	89	22	73	15	97	14
PCB101-C_{13}	98	14	86	18	110	17	90	21	69	10	95	11

[a] Data for 231 air, 83 dust/soil, and 126 wipe samples were excluded because of interference or matrix effect.
[b] Data for 97 air, 210 dust/soil. 147 wipe, 36 liquid food, and 36 solid food samples were excluded because of interference or matrix effect.
[c] Data for 24 dust/soil and 39 solid food samples were excluded because of matrix effect or interference.

Table 6.2.14 Results for Surrogate Recovery Standards for Acidic Pollutants - North Carolina

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food	
Typical spike level, ng	50		50		50		50		50	
Number of QC samples	355		359		290		332		379	
Percent of field samples	120		120		110		110		130	
Percent Recovery, %										
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
2,4-D-C_{13} [a]	79	15	79	14	75	11	75	14	91	16

[a] Data for 11 air samples were excluded because of matrix effect.

Table 6.2.15 Results for Surrogate Recovery Standards for Urine Analysis - North Carolina

Pollutant	Urine	
Typical spike level, ng	20	
Number of QC samples	564	
Percent of field samples	120	
	Percent Recovery, %	
	mean	SD
2,4-D-C_{13}	91	18

Table 6.2.16 Results for Blank Samples Having Detectable Neutral Pollutants - North Carolina

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
	MB	FB	MB	FB	MB	FB	MB	FB	MB	FB	MB	FB
Number of QC samples	17	12	23	12	15	13	8	12	7	12	2	0
Percent of field samples	5.6	3.9	7.7	4.0	5.2	4.5	4.9	7.4	4.2	7.2	11	0
	Concentration											
	ng/m^3		ng/g		ng/sample		ng/mL		ng/g		ng/m^2	
OP Pesticides	median	SD	median	SD	median	SD	median	SD	median	SD	median	SD
Chlorpyrifos	0.06	0.01	- [a]	-	-	-	-	-	-	-	-	-
Pyrethroid Pesticides												
cis-Permethrin	0.06	0.03	-	-	-	-	0.003	0.03	-	-	-	-
trans-Permethrin	-	-	-	-	-	-	0.003	0.07	-	-	-	-
Phthalates												
Benzylbutylphthalate	28	78	41	96	360	490	9.8	43	36	86	7000	1500
di-*n*-Butylphthalate	24	21	38	59	300	500	42	46	94	130	9000	8800
Phenols												
Bisphenol-A	-	-	-	-	7.1	15	-	-	-	-	-	-

a. - denotes not detected in all blanks.

Table 6.2.17 Results for Blank Samples Having Detectable Acidic Pollutants/Metabolites - North Carolina

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food	
	MB	FB	MB	FB	MB	FB	MB	FB	MB	FB
Number of QC samples	19	12	15	12	12	11	7	12	17	12
Percent of field samples	6.3	4.0	5.1	4.0	4.7	4.3	2.5	4.2	5.7	4.0
	Concentration									
	ng/m^3		ng/g		ng/sample		ng/mL		ng/g	
	median	SD	median	SD	median	SD	median	SD	median	SD
OP Metabolites										
3,5,6-TCP	0.06	0.01	1.4	0.56	0.71	0.88	-	-	0.09	0.03
Phenols										
PCP	0.06	1.1	- [a]	-	-	-	-	-	-	-

a. - denotes not detected in all blanks.

Table 6.2.18 Results for Water Samples - North Carolina

Pollutant	Drinking Water Samples							
	Duplicate		Analytical Duplicate		MSS		Blank	
							MB	FB
Number of QC	28		28		16		15	13
Percent of field	18		18		10		9.7	8.4
	Relative Percent Difference, %		Relative Percent Difference, %		Percent Recovery, %		Concentration, ng/mL	
	mean	SD	mean	SD	mean	SD	median	SD
Atrazine	2.2	3.5	2.3	5.1	84	20	0.01	0.02

6.2.4.2.2 Ohio For the OH study, results of the %RPD of duplicate samples for neutral pollutants, acidic pollutants/metabolites, and pollutants/metabolites in urine are summarized in Tables 6.2.19, 6.2.20, and 6.2.21, respectively. The mean of the %RPD was between 0% and 18% for all duplicate samples, except for the two phthalates. The mean of the %RPD for the two phthalates ranged from 7.1% to 38%. Results of the %RPD of duplicate GC/MS analyses are summarized in Tables 6.2.22 to 6.2.24. As expected, %RPD values from the duplicate GC/MS analyses were smaller than those from the duplicate samples.

Recovery data for the OH matrix spike samples are summarized in Tables 6.2.25 to 6.2.27. Recovery data of SRSs are summarized in Tables 6.2.28 to 6.2.30. With few exceptions, quantitative matrix spike and SRS recoveries were obtained for the target compounds in all sample media. Mean recoveries ranged from 70±16% to 130±23% for neutral pollutants, from 71±8.2% to 100±11% for acidic pollutants/metabolites. Because of the high background levels found in the nonspiked blank sample media as well as the high levels found in field samples, the spiked levels of the two phthalates were not high enough in most of the matrix spike samples. As a result, satisfactory recoveries could not be obtained. For the same reason, satisfactory recoveries for diazinon, PAHs, and *trans*-permethrin could not be obtained in one matrix spike sample. Interference peaks were observed for bisphenol-A, cyfluthrin, and *cis*-permethrin in some samples. Recovery of IMP was not acceptable (<50%) in liquid food, solid food, and urine samples. This was mainly because the analytical method developed for the other OP metabolite, 3,5,6-TCP, was also used to measure IMP, but was found to be inadequate to measure IMP in some matrices. Different analytical methods need to be developed and evaluated for quantitative determination of IMP in these sample media.

Quantitative recoveries for the SRSs including p,p'-DDE-d_4, dibenz[*a*,*h*]anthracene-d_{14}, PCB101-C_{13}, and 2,4-D-C_{13} were obtained in most OH field samples. Interference peaks were observed for the benzylbutylphthalate-d_4 and bisphenol-A-d_6, in some air, dust, soil, and wipe samples; satisfactory recoveries for these SRSs were not obtained.

Results of the OH field blanks and laboratory blanks are summarized in Tables 6.2.31 to 6.2.33. Note that the reported median and SD values were from the combined field blanks and laboratory method blanks. The median concentrations of the target pollutants/metabolites were below or close to the method detection limits. Measurable amounts of the two phthalates were found in the field blanks and laboratory method blanks in all media, and cis- and trans-permethrin were found in air blanks. Therefore, background-corrected data for these samples were used for the statistical analysis discussed in Chapter 8 of this report.

Table 6.2.19 Results for Duplicate Samples for Neutral Pollutants - Ohio

Pollutant	Dust/Soil		Liquid Food		Solid Food	
Number of QC samples	22		8		10	
Percent of field samples	7.2		4.8		5.9	
	Relative Percent Difference, %					
OP Pesticides	mean	SD	mean	SD	mean	SD
Chlorpyrifos	4.8	8.9	0.79	1.6	9.6	5
Diazinon	7.8	10	-[a]	-	1.6	2.5
OC Pesticides						
Aldrin	-	-	-	-	-	-
alpha-Chlordane	3.9	5.6	-	-	-	-
gamma-Chlordane	4.2	5.2	-	-	-	-
p,p'-DDE	3.8	7.7	-	-	4.8	4.2
p,p'-DDT	1.9	4.4	-	-	-	-
Dieldrin	3.1	6.9	-	-	-	-
Endrin	0.18	0.60	-	-	-	-
Heptachlor	-	-	-	-	-	-
Lindane	-	-	-	-	-	-
Pentachloronitrobenzene	-	-	-	-	-	-
Pyrethroid Pesticides						
Cyfluthrin	3.7	6.3	-	-	-	-
cis-Permethrin	3.3	4.0	-	-	2.3	2.4
trans-Permethrin	2.8	3.5	-	-	3.9	4.2
PAHs						
Benz[*a*]anthracene	18	14	-	-	0.37	0.84
Benzo[*a*]pyrene	13	12	-	-	0.63	1.4
Benzo[*b*]fluoranthene	8.3	7.7	-	-	3.7	6.6
Benzo[*e*]pyrene	13	9.4	-	-	-	-
Benzo[*ghi*]perylene	11	8.5	-	-	-	-
Benzo[*k*]fluoranthene	5.8	5.3	-	-	0.36	0.50
Chrysene	14	10	-	-	2.5	3.5
Dibenz[*a,h*]anthracene	10	8.9	-	-	-	-
Indeno[1,2,3-*cd*]pyrene	11	7.0	-	-	-	-
Phthalates						
Benzylbutylphthalate	22	34	29	28	30	28
di-*n*-Butylphthalate	15	11	38	17	7.1	2.8
Phenols						
Bisphenol-A	2.3	3.9	4.7	9.3	9.6	12
Nonylphenol	-	-	-	-	-	-
PCBs						
PCB 44	0.79	1.7	NM	-	-	-
PCB 52	1.4	2.4	NM	-	-	-
PCB 70	1.1	2.9	NM	-	-	-
PCB 77	-	-	NM	-	-	-
PCB 95	4.1	6.5	NM	-	-	-
PCB 101	2.1	3.2	NM	-	-	-
PCB 105	0.55	1.8	NM	-	-	-
PCB 110	2.3	4.3	NM	-	-	-
PCB 118	1.1	1.6	NM	-	-	-
PCB 138	1.2	3.4	NM	-	-	-
PCB 153	3.3	5.4	NM	-	-	-
PCB 180	0.73	2.4	NM	-	-	-

[a] - denotes not detected in all duplicate samples.
[b] NM denoted that PCBs were not measured in liquid food samples.

Table 6.2.20 Results for Duplicate Samples for Acidic Pollutants/Metabolites - Ohio

Pollutant	Dust/Soil		Liquid Food		Solid Food	
Number of QC samples	20		22		16	
Percent of field samples	6.7		7.6		5.4	
	Relative Percent Difference, %					
OP Metabolites	mean	SD	mean	SD	mean	SD
IMP	3.5	5.3	1.5	5.0	7.1	5.3
3,5,6-TCP	5.0	3.4	2.1	2.4	6.3	5.6
Acid Herbicides						
dicamba	1.3	2.8	- [a]	-	2.0	5.6
2,4-D	5.2	7.8	-	-	1.9	3.0
2,4,5-T	0.66	2.1	-	-	-	-
Phenols						
PCP	4.2	4.4	-	-	0.33	0.93

a. - denotes not detected in all duplicate samples.

Table 6.2.21 Results for Duplicate Samples for Urine Analysis - Ohio

Pollutant	Urine	
Number of QC samples	26	
Percent of field samples	5.7	
	Relative Percent Difference, %	
OP Metabolites	mean	SD
IMP	- [a]	-
3,5,6-TCP	4.8	6.1
Acid Herbicides		
2,4-D	4.1	4.0
PAH Metabolites		
1-Hydroxybenz[*a*]anthracene	0.18	0.44
3-Hydroxychrysene	-	-
Phenols		
PCP	4.9	3.4

a. - denotes not detected in all duplicate samples.

Table 6.2.22 Results for Duplicate Analyses of the Same Sample Extract for Neutral Pollutants - Ohio

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
	PCB	Others	PCB	Others	PCB	Others	PCB	Others	PCB	Others	PCB	Others
Number of QC samples	32	34	44	30	54	38	NM [a]	18	28	24	4	4
Percent of field samples	10	11	15	10	19	14	-	11	16	14	29	29
	Relative Percent Difference, %											
OP Pesticides	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Chlorpyrifos	2.0	2.6	2.3	3.4	2.3	2.8	-	-	2.5	3.7	5.7	8.1
Diazinon	3.7	5.3	3.7	4.4	1.4	2.9	-	-	0.23	0.57	1.3	1.9
OC Pesticides												
Aldrin	0.05	0.20	0.11	0.42	- [b]	-	-	-	-	-	-	-
alpha-Chlordane	3.0	3.7	3.4	2.9	1.8	4.2	-	-	0.66	2.3	-	-
gamma-Chlordane	4.1	4.0	3.5	3.6	1.8	3.2	-	-	0.66	2.3	-	-
p,p'-DDE	-	-	2.7	3.2	-	-	-	-	1.5	1.8	-	-
p,p'-DDT	-	-	2.7	4.6	0.10	0.43	-	-	-	-	-	-
Dieldrin	0.18	0.74	0.57	1.6	-	-	-	-	0.35	1.2	9.0	13
Endrin	0.11	0.30	0.04	0.15	-	-	-	-	-	-	-	-
Heptachlor	1.2	2.7	0.54	1.5	-	-	-	-	0.06	0.21	-	-
Lindane	-	-	0.40	1.6	-	-	-	-	-	-	-	-
Pentachloronitrobenzene	0.80	3.0	-	-	-	-	-	-	-	-	-	-
Pyrethroid Pesticides												
Cyfluthrin	-	-	2.3	4.0	0.19	0.57	-	-	-	-	-	-
cis-Permethrin	3.5	4.1	3.6	3.6	2.3	3.4	-	-	-	-	2.4	1.7
trans-Permethrin	1.6	2.4	2.4	1.9	4.3	4.9	-	-	-	-	3.4	0.50
PAHs												
Benz[*a*]anthracene	2.0	3.7	2.6	1.9	2.0	2.4	-	-	0.30	0.81	3.4	4.4
Benzo[*a*]pyrene	0.31	0.71	2.3	1.8	1.7	2.1	-	-	0.07	0.23	6.7	2.2
Benzo[*b*]fluoranthene	1.2	2.6	3.7	2.7	2.5	3.6	-	-	2.2	4.8	3.6	4.2
Benzo[*e*]pyrene	2.2	3.7	2.8	2.2	2.9	3.3	-	-	0.66	2.0	4.6	4.5
Benzo[*ghi*]perylene	1.5	3.5	3.6	2.7	2.6	2.3	-	-	-	-	4.2	0.34
Benzo[*k*]fluoranthene	0.88	1.8	3.3	3.5	3.3	3.3	-	-	0.12	0.42	2.8	0.98
Chrysene	1.8	2.6	2.8	3.2	2.4	2.2	-	-	0.85	2.5	1.7	1.0
Dibenz[*a,h*]anthracene	-	-	4.9	4.1	3.4	6.3	-	-	-	-	-	-
Indeno[1,2,3-*cd*]pyrene	0.83	1.6	4.3	4.0	3.7	3.5	-	-	-	-	2.2	0.44

Table 6.2.22 Results for Duplicate Analyses of the Same Sample Extract for Neutral Pollutants - Ohio (cont.)

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
Phthalates	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Benzylbutylphthalate	11	21	6.1	9.8	2.6	3.1	3.8	4.6	2.4	1.8	1.3	0.79
di-*n*-Butylphthalate	9.1	26	7.5	13	1.6	2.7	3.3	4.0	1.2	0.95	0.87	0.42
Phenols												
Bisphenol-A	3.5	4.1	2.1	3.6	3.4	3.8	2.6	3.2	3.8	1.9	2.9	0.58
Nonylphenol	-	-	-	-	-	-	-	-	-	-	-	-
PCBs												
PCB 44	0.26	1.0	0.51	1.7	0.41	1.5	NM	-	-	-	-	-
PCB 52	4.7	5.4	1.5	2.4	0.67	1.8	NM	-	0.23	0.87	8.5	4.0
PCB 70	0.71	1.5	0.72	1.5	1.2	3.4	NM	-	-	-	0.62	0.87
PCB 77	-	-	-	-	-	-	NM	-	-	-	-	-
PCB 95	1.7	2.8	1.9	3.6	0.57	2.6	NM	-	-	-	-	-
PCB 101	0.78	2.7	0.83	1.4	0.43	1.6	NM	-	-	-	3.9	5.4
PCB 105	-	-	0.29	1.3	0.11	0.58	NM	-	-	-	-	-
PCB 110	0.27	1.1	1.4	2.5	0.25	0.84	NM	-	-	-	4.3	4.8
PCB 118	-	-	0.89	1.8	0.25	0.98	NM	-	-	-	-	-
PCB 138	-	-	0.67	1.6	-	-	NM	-	-	-	-	-
PCB 153	-	-	1.7	3.6	-	-	NM	-	-	-	-	-
PCB 180	-	-	0.72	1.8	-	-	NM	-	-	-	-	-

[a] NM denotes that PCBs were not measured in liquid food samples.
[b] - denotes not detected in all duplicate GC/MS analyses.

Table 6.2.23 Results for Duplicate Analyses of the Same Sample Extract for Acidic Pollutants/Metabolites - Ohio

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food	
	silylate	methylate	silylate	methylate	silylate	methylate	silylate	methylate	silylate	methylate
Number of QC samples	28	26	28	42	30	20	24	30	16	16
Percent of field samples	9.2	8.5	9.3	14	12	7.9	8.3	10	5.4	5.4
Relative Percent Difference, %										
OP Metabolites	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
IMP	3.1	3.10	1.9	2.8	1.5	2.8	0.68	1.7	4.1	5.1
3,5,6-TCP	5.0	6.5	1.1	1.3	3.6	2.9	0.85	1.5	2.9	2.3
Acid Herbicides										
Dicamba	0.03	0.10	1.1	2.4	0.05	0.14	-	-	0.19	0.53
2,4-D	2.7	5.7	2.6	4.2	1.2	1.7	-	-	0.32	0.52
2,4,5-T	- [a]	-	-	0.01	-	-	-	-	-	-
Phenols										
PCP	2.9	4.2	1.8	1.7	1.6	2.3	0.38	1.5	0.06	0.16

[a] - denotes not detected in all duplicate GC/MS analyses.

Table 6.2.24 Results for Duplicate Analyses of the Same Sample Extract for Urine - Ohio

Pollutant	Urine	
Number of QC samples	56	
Percent of field samples	12	
Relative Percent Difference, %		
OP Metabolites	mean	SD
IMP	0.05	0.21
3,5,6-TCP	1.8	1.6
Acid Herbicides		
2,4-D	3.1	2.8
PAH Metabolites		
1-Hydroxybenz[*a*]anthracene	- [a]	-
3-Hydroxychrysene	-	-
Phenols		
PCP	4.9	3.8

[a] - denotes not detected in all duplicate GC/MS analyses.

Table 6.2.25 Results for Matrix Spike Samples for Neutral Pollutants - Ohio

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food	
Typical spike level, ng	50		20		20		25		50	
Number of QC samples	19		11		7		6		7	
Percent of field samples	6.2		3.7		2.5		3.6		4.1	
	Percent Recovery, %									
OP Pesticides	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Chlorpyrifos	97	13	81	6.8	110	12	89	11	100	17
Diazinon [a]	77	13	77	7.8	95	120	72	13	78	12
OC Pesticides										
Aldrin	84	9.8	81	12	91	14	90	8.4	93	14
alpha-Chlordane	91	12	72	4.0	95	12	73	9.3	78	8.3
gamma-Chlordane	91	11	75	7.3	96	15	72	9.4	76	6.7
p,p'-DDE	95	12	76	5.7	93	15	81	11	77	13
p,p'-DDT	96	23	88	13	110	15	89	12	110	17
Dieldrin	87	12	92	15	93	15	90	6.0	93	13
Endrin	94	12	82	8.5	110	10	90	10	100	9.8
Heptachlor	90	15	95	13	100	16	83	13	100	7.2
Lindane	86	9.1	81	11	120	7.3	87	12	110	12
Pentachloronitrobenzene	87	11	82	16	110	10	100	16	120	14
Pyrethroid Pesticides										
Cyfluthrin [b]	97	19	100	14	100	15	71	18	110	16
cis-Permethrin [c]	100	17	110	30	99	12.	87	19	110	27
trans-Permethrin [d]	88	11	86	7.1	97	1.8	68	27	85	17
PAHs [e]										
Benz[*a*]anthracene	89	17	87	21	95	16	91	16	100	24
Benzo[*a*]pyrene	76	18	90	15	95	19	91	13	100	13
Benzo[*b*]fluoranthene	88	16	95	24	97	17	96	12	92	13
Benzo[*e*]pyrene	75	12	82	14	92	17	81	7.8	82	11
Benzo[*ghi*]perylene	72	12	90	15	88	17	89	14	100	17
Benzo[*k*]fluoranthene	84	19	86	8.8	93	15	99	7.9	96	17
Chrysene	85	14	90	18	91	15	78	12	83	17
Dibenz[*a,h*]anthracene	74	15	79	6.1	92	16	100	16	100	20
Indeno[1,2,3-*cd*]pyrene	70	16	87	13	91	19	100	18	100	16

Table 6.2.25 Results for Matrix Spike Samples for Neutral Pollutants - Ohio (cont.)

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food	
Phthalates	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Benzylbutylphthalate [f]	-	-	80	12	-	-	-	-	120	15
di-*n*-Butylphthalate [g]	-	-	91	11	-	-	-	-	76	5.8
Phenols										
Bisphenol-A [h]	78	10	567	4.2	110	13	97	24	130	23
Nonylphenol	86	12	76	20	100	12	100	19	130	12
PCBs [i]										
PCB 44	89	13	75	5.1	80	14	-	-	84	12
PCB 52	88	11	78	9.5	87	8.7	-	-	86	11
PCB 70	93	14	76	6.0	87	8.3	-	-	90	11
PCB 77	92	15	83	14	90	17	-	-	100	13
PCB 95	87	14	72	7.2	81	11	-	-	78	12
PCB 101	90	12	73	7.7	87	8.6	-	-	86	12
PCB 105	99	14	79	7.4	88	11	-	-	100	19
PCB 110	93	12	73	7.1	88	9.0	-	-	91	13
PCB 118	97	13	74	6.3	87	13	-	-	98	15
PCB 138	94	12	78	8.4	86	10	-	-	94	14
PCB 153	93	12	76	7.5	86	11	-	-	95	15
PCB 180	99	15	78	8.3	85	12	-	-	98	17

[a] Data for diazinon in one dust/soil sample was excluded because of low spike level.
[b] Data for two dust/soil samples were excluded because of interference.
[c] Data for eight dust/soil samples were excluded because of interference or low spike level.
[d] Data for one dust/soil sample was excluded because of low spike level.
[e] Data for all target PAHs in one dust/soil sample was excluded because of low spike level.
[f] Data for air, wipe, and liquid food can not be obtained because of low spike level; data for seven dust/soil, six liquid food, and five solid food samples were excluded because of low spike level or matrix effect.
[g] Data for air, wipe, and liquid food can not be obtained because of low spike level; data for eight dust/soil, six liquid food, and five solid food samples were excluded because of low spike level or matrix effect.
[h] Data for two air samples, eight dust/soil samples were excluded because of matrix effect.
[i] PCBs were not measured in liquid food samples.

Table 6.2.26 Results for Matrix Spike Samples for Acidic Pollutants/Metabolites - Ohio

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
Typical spike level, ng	50		50		50		50		50		50	
Number of QC samples	14		8		9		11		9		1	
Percent of field samples	4.6		2.7		3.5		3.8		3.0		25	
	Percent Recovery, %											
OP Metabolites	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean [a]	SD
IMP	93	12	63	35	79	13	6.6	4.6	10	5.9	59	NA
3,5,6-TCP	86	12	82	8.7	86	14	79	13	86	17	56	NA
Acid Herbicides												
Dicamba	77	10	72	11	79	15	82	9.9	78	6.0	26	NA
2,4-D	80	9.3	71	8.2	82	9.9	83	11	85	8.2	51	NA
2,4,5-T	85	8.8	81	12	83	11	84	6.4	86	9.1	51	NA [b]
Phenols												
PCP	77	7.0	86	12	79	5.9	84	18	84	10	75	NA

[a] The reported mean value for the PUF sample was the recovery data of the one matrix spike PUF sample analyzed.
[b] NA denotes not applicable.

Table 6.2.27 Results for Matrix Spike for Urine Analysis - Ohio

Pollutant	Urine	
Typical spike level, ng	25	
Number of QC samples	14	
Percent of field samples	3.0	
	Percent Recovery, %	
OP Metabolites	mean	SD
IMP [a]	5.0	2.3
3,5,6-TCP	96	10
Acid Herbicides		
2,4-D	98	20
PAH Metabolites		
1-Hydroxybenz[*a*]anthracene	95	16
3-Hydroxychrysene	100	11
Phenols		
PCP	96	18

[a] Low recoveries were obtained for IMP because the analytical method used was developed for 3,5,6-TCP, not IMP.

Table 6.2.28 Results for Surrogate Recovery Standards for Neutral Pollutants - Ohio

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
Typical spike level, ng	50		20		20		25		50		20	
Number of QC samples	360		347		317		192		198		17	
Percent of field samples	120		120		110		110		120		120	
	Percent Recovery, %											
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Benzylbutylphthalate-d_4 [a]	120	38	100	28	110	28	61	12	63	15	110	8.9
Bisphenol-A-d_6 [b]	92	25	65	14	100	13	97	19	120	20	65	6.5
Dibenz[*a*,*h*]anthracene-d_{14}	80	18	75	16	92	16	98	19	100	21	75	12
p,p'-DDE-d_4	98	18	82	31	94	15	80	18	75	12	100	14
PCB101-C_{13}	94	16	78	11	89	11	NM [c]	-	93	19	95	8.5

[a] Data for 85 liquid food and 119 solid food were excluded because of matrix effect.
[b] Data for 256 dust/soil, 75 wipe, 22 solid food, and 14 PUF were excluded because of interference or matrix effect.
[c] NM denotes that PCBs were not measured in liquid food samples.

Table 6.2.29 Results for Surrogate Recovery Standards for Acidic Pollutants - Ohio

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
Typical spike level, ng	50		50		50		50		50		70	
Number of QC samples	357		350		281		336		333		5	
Percent of field samples	120		120		110		120		110		120	
	Percent Recovery, %											
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
2,4-D-C_{13}	80	15	81	11	82	10	90	13	88	12	53	1.8

Table 6.2.30 Results for Surrogate Recovery Standards for Urine Analysis - Ohio

Pollutant	Urine	
Typical spike level, ng	20	
Number of QC samples	518	
Percent of field samples	110	
	Percent Recovery, %	
	mean	SD
2,4-D-C_{13}	95	20

Table 6.2.31 Results for Blank Samples with Detectable Neutral Pollutants - Ohio

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
	MB	FB	MB	FB	MB	FB	MB	FB	MB	FB	MB	FB
Number of QC samples	18	14	11	14	12	14	5	14	4	14	1	1
Percent of field samples	5.9	4.6	3.7	4.7	4.3	5.0	3.0	8.3	2.3	8.2	7.1	7.1
Concentration												
	ng/m^3		ng/g		ng/sample		ng/mL		ng/g		ng/m^2	
OP Pesticides	median	SD	median	SD	median	SD	median	SD	median	SD	median	SD
Chlorpyrifos	0.06	0.01	-	-	-	-	-	-	-	-	-	-
OC Pesticides												
p,p'-DDT	- [a]	-	-	-	-	-	0.003	0.03	-	-	-	-
Pyrethroid Pesticides												
Cyfluthrin	0.62	0.08	-	-	-	-	-	-	-	-	-	-
cis-Permethrin	0.06	0.52	-	-	-	-	0.003	0.21	-	-	-	-
trans-Permethrin	0.06	0.44	-	-	-	-	0.003	0.22	-	-	-	-
PAHs												
Benz[*a*]anthracene	0.06	0.02	-	-	-	-	-	-	-	-	-	-
Chrysene	0.06	0.01	-	-	-	-	-	-	-	-	-	-
Phthalates												
Benzylbutylphthalate	27	50	66	47	360	1400	14	12	10	12	4100	4800
di-*n*-Butylphthalate	44	43	130	170	760	1800	25	7.2	66	41	18000	23000
Phenols												
Bisphenol-A	0.62	0.55	-	-	7.1	11	0.03	0.67	-	-	388	510
PCBs												
PCB 44	0.03	0.02	-	-	-	-	-	-	-	-	-	-
PCB 52	0.03	0.02	-	-	0.71	0.83	-	-	-	-	-	-
PCB 70	0.03	0.03	-	-	0.71	0.83	-	-	-	-	-	-
PCB 110	0.03	0.01	-	-	0.71	0.83	-	-	-	-	-	-

[a] - denotes that the pollutant was not detected in all the blanks.

Table 6.2.32 Results for Blank Samples with Detectable Acidic Pollutants/Metabolites - Ohio

Pollutant	Air		Dust/Soil		Wipes		Liquid Food		Solid Food		PUF	
	MB	FB	MB	FB	MB	FB	MB	FB	MB	FB	MB	FB
Number of QC samples	21	14	11	14	9	14	8	14	9	14	-	1
Percent of field samples	6.9	4.6	3.7	4.7	3.2	5.0	2.8	4.8	3.0	4.7	-	25
	Concentration											
	ng/m^3		ng/g		ng/sample		ng/mL		ng/g		ng/m^2	
OP Metabolites	median	SD	median	SD	median	SD	median	SD	median	SD	median	SD
IMP	0.06	0.01	-	-	-	-	-	-	-	-	-	-
3,5,6-TCP	0.06	0.03	-	-	0.71	0.89	-	-	0.09	0.05	-	-
Acid Herbicides												
2,4-D	0.12	0.03	- [a]	-	1.4	1.7	-	-	-	-	-	-
Phenols												
PCP	0.12	0.27	-	-	-	-	-	-	-	-	-	-

[a] - denotes that the pollutant was not detected in all the blanks.

Table 6.2.33 Results for Blank Samples with Detectable Urine Pollutants - Ohio

Pollutant	Urine	
	MB	FB
Number of QC samples	16	14
Percent of field samples	3.5	3.0
	Concentration, ng/mL	
	median	SD
OP Metabolites		
3,5,6-TCP	0.71	0.18

The QC data for the OH water samples are summarized in Table 6.2.34. The overall method precision was very good. The mean of the RPD of duplicate water samples was 2.1 ± 3.4%; similar results were obtained from the duplicate GC/MS analyses. The average recovery of the matrix spike samples was 79 ± 4.7%. Trace amounts of atrazine were found in some of the blank samples.

Table 6.2.34 Results of Analysis of Water Samples - Ohio

Pollutant	Drinking Water Samples							
	Duplicate		Analytical Duplicate		MSS		Blank	
							MB	FB
Number of QC samples	8		26		5		5	14
Percent of field samples	5.1		17		3.2		3.2	8.9
	Relative Percent Difference, %		Relative Percent Difference, %		Percent Recovery, %		Concentration, ng/mL	
	mean	SD	mean	SD	mean	SD	median	SD
Atrazine	2.1	3.4	2.3	1.8	79	4.7	0.01	0.001

6.3 Evaluation

Due to budget constraints, different analytical methods could not be used for each compound class. Instead, the OP and OC pesticides, pyrethroid pesticides, PAHs, phthalates, phenols except for PCP, PCBs, and triazine were grouped as neutral pollutants, and the acid herbicides, PCP and metabolites for OP pesticides, pyrethroid pesticides, and PAHs were grouped as acid pollutants/metabolites.

Two carbamate pollutants, propoxur and bendiocarb, were not included in the day care pilot studies, and were added later to the CTEPP study design at the suggestion of the EPA Office of Pesticide Programs, in hopes that the CTEPP methods might be able to detect these compounds (7-10). However, the analytical methods used in the CTEPP study were not tested for these two compounds. Unfortunately, these two pollutants decompose partially on the GC column and interference compounds co-eluted with both propoxur and bendiocarb. Therefore, useful data were not obtained for these two compounds.

Atrazine could be measured accurately in water samples, but there were interference problems in other sample media. For air, dust, soil, and wipe samples, there was an interference compound that eluted at the same retention time as atrazine on the GC column, and which also had the same ion ratio of the monitored ions as those observed for atrazine. This was initially observed in the air samples, when extremely high concentrations (>1000 ng/mL) were detected for what was believed to be atrazine. The sample extracts were re-analyzed using GC/MS in full mass scan mode in an attempt to confirm the presence of atrazine in these sample extracts. The full mass scan results showed that an interference compound, which was an unsaturated aliphatic hydrocarbon, eluted at the same retention time and had the same monitored ion ratio as did atrazine. Therefore, atrazine was measured only in drinking water samples.

Interference peaks were also observed for cyfluthrin, *cis*-permethrin, bisphenol-A-d_6, and benzylbutylphthalate-d_4 in some samples. These interference peaks affected only the quantification of the SRSs, benzylbutylphthalate-d_4 and bisphenol-A-d_6, and did not affect the quantification of the native chemicals benzylbutylphthalate and bisphenol-A. If the interference components were not completely resolved from the peaks of target pollutants, estimated values were obtained and reported. These data were coded with "INT" in the database to show the presence of the interferences. Note that the interference peak for *cis*-permethrin became insignificant when the concentrations of this compound exceeded 100 to 500 ng/mL, depending upon the sample. In these cases, the INT codes were not reported in the database. In some samples, interferences were observed for one of the surrogate recovery standard (SRS), bisphenol-A-d6, but not for the native compound bisphenol-A. Similar interferences were observed for benzylbutylphthalate-d_6, but not for benzylbutylphthalate.

It is not surprising that phthalates were found in field blanks and laboratory blanks. Background levels varied greatly among different sample matrices. Phthalates were present in the analytical-grade solvents that were used for extracting samples and cleaning up sample extracts. Plastic-related materials were used in the disposal pipette holders and in the pre-packed solid phase extraction (SPE) columns that were used to clean up sample extracts. Depending upon the sample media, types of solvent used, and cleanup method employed, the background levels of phthalates varied. In general, the phthalate contamination increased with sample handling and number of cleanup steps. Also, in food samples, the elution band of the phthalates on the GPC column included many fatty acids and fatty acid esters that hindered low-level detection of pyrethroids such as cyfluthrin. The GPC fractions had to be cleaned up further, using ENVI-Carb columns for the food samples, in order to measure cyfluthrin.

The determination of a diazinon metabolite, IMP, in the environmental and personal samples was added late in the OH field study. We used the same analytical methods for TCP to measure IMP in these samples. Results of the matrix spike samples showed that IMP were quantatively measured in air, dust, soil, wipe but not in urine, solid food and liquid food samples. We have identified that IMP was lost during the liquid-liquid partitioning step. The overall recoveries of IMP in these samples were less than 10%, no statistical analyses were performed on these data.

6.4 Recommendations

We recommend evaluation of cleanup methods and/or different detection methods such as liquid chromatography (LC)/MS to determine carbamates in multimedia samples for future studies. In an on-going Battelle study for US EPA, we developed an analytical method for the determination of carbamates in water samples. This method consists of SPE extraction of water samples into acetonitrile (ACN) and LC/MS analysis of the ACN extracts.

We recommend evaluation of cleanup methods such as use of a C18 SPE column or an immunoaffinity (IA) purification column to determine atrazine in multimedia samples. In an on-going Battelle study for US EPA, we developed an IA column for atrazine, established the elution

profile of atrazine for the IA column. Preliminary results suggest that the IA column is an effective cleanup method for analysis of atrazine in dust and soil samples.

Different SRSs should be evaluated for phthalates and bisphenol-A to minimize the interference peaks observed in multimedia samples for future studies.

In a recent Battelle internal research and development study, we developed an analytical method that can provide quantitative recoveries of IMP from urine samples. We therefore recommend that this new analytical method be evaluated and refined as necessary for determining IMP in multimedia samples in future studies.

As noted earlier, phthalates were found in the field blanks and in the laboratory blanks. In this study, the phthalate contamination increased with increased sample handling and with the number of cleanup steps. For future studies, we recommend a different approach to measurement of phthalates in multimedia samples. Since phthalates are typically present at much higher concentrations than the other target pollutants in multimedia samples, we would conduct GC/MS analysis of the phthalates in dilute sample extracts prior to any cleanup steps for the neutral compound analyses, as a separate analysis. This approach would eliminate much of the exacting and time-consuming sample preparation work associated with limiting phthalate contamination from sample handling. The GC/MS analysis of the phthalates would include both the m/z 149 ion for quantification of low concentration pollutants, and the molecular ion for quantification of pollutants at higher levels.